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14. ABSTRACT In an effort to understand the details of shock compression of molecules used in energetic materials, we have conducted femtosecond laser experiments where a monolayer of energetic material simulants such as nitrobenzenethiol are subjected to a laser-driven shock wave while vibrational spectroscopy is used to probe their response. A monolayer is needed to attain the high time and space resolution necessary to make a detailed comparison to simulations. In support of the shock compression measurements, we also studied the response to					
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Report Title

Final report: What is a shock wave to a molecule?

ABSTRACT

In an effort to understand the details of shock compression of molecules used in energetic materials, we have conducted femtosecond laser experiments where a monolayer of energetic material simulants such as nitrobenzenethiol are subjected to a laser-driven shock wave while vibrational spectroscopy is used to probe their response. A monolayer is needed to attain the high time and space resolution necessary to make a detailed comparison to simulations. In support of the shock compression measurements, we also studied the response to flash heating and static high pressure up to 10 GPa.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. Carter, J. A., Wang, Z., Fujiwara, H., and Dlott, D. D., Ultrafast excitation of molecular adsorbates on flash-heated gold surfaces, J. Phys. Chem. A 113, 12105–12114 (2009).
2. Lagutchev, A., Brown, K. E., Carter, J. A., Fu, Y., Fujiwara, H., Wang, Z., and Dlott, D. D., Ultrafast vibrational spectroscopy of shock compression with molecular resolution, AIP Conf. Proc. 1195, 301-304 (2010).

Number of Papers published in peer-reviewed journals: 2.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. APS Topical Meeting on Shock Compression in Condensed Matter, Nashville, TN, June 2009, "Ultrafast vibrational spectroscopy of shock compression with molecular resolution: energetic material simulants".
2. Telluride workshop on Vibrational Dynamics, Telluride, CO, July 2009, "Vibrational energy transport in molecules".
3. Pinhead Institute Town Talk, Telluride Conference Center, Telluride, CO, July 2009, "The science of explosions: Blowing things up for fun, profit, war and medicine".
4. Gordon Conference on Vibrational Dynamics at Surfaces, Proctor Academy, Andover, NH, Aug. 2009, "Dynamics at interfaces probed by time-resolved sum-frequency spectroscopy".
5. 21st Century Needs and Challenges of Compression Science Workshop, Santa Fe, NM, Sept. 2009, "Shock compression of molecules with high time and space resolution"
6. North Carolina State University, Jan. 2010, "Vibrational energy in materials with high time and space resolution".

Number of Presentations: 6.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Number of Manuscripts:0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Jeffrey A. Carter	0.25
Yuanxi Fu	0.25
FTE Equivalent:	0.50
Total Number:	2

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Alexei A. Lagutchev	0.80
FTE Equivalent:	0.80
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Dana D Dlott	0.00	No
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

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Total Number:

Names of other research staff

NAME

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Sub Contractors (DD882)

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Statement of problem. Molecular simulations of shock compression of energetic materials provide compelling pictures of molecules with atomic time and space resolution. To match this level of detail in experiment, we have developed ultrafast shock compression of molecular monolayers. Only with a shock gauge layer one molecule in thickness is it possible to obtain atomic-scale resolution. However high sensitivity is needed to probe such thin layers. Self-assembled monolayers (SAMs) used here have a thiol -SH anchor group to form dense highly-ordered 2D lattices on Au or Ag. Functional groups of the SAMs are probed with a nonlinear coherent vibrational spectroscopy termed sum-frequency generation (SFG), where a broadband femtosecond IR pulse is combined with an 800 nm visible pulse.

Sample target arrays were fabricated on 50 x 50 x 1.6 mm³ glass substrates. As illustrated in Fig. 1a, a shock target array has a Cr adhesion layer, a Ni insulation layer and an Au layer for the SAM. The Cr layer was typically 1 nm thick. After the SAM was deposited on Au, a few drops of contact liquid were added and a 3 mm thick CaF₂ IR confinement window was pressed over the liquid. The contact liquid was deuterated ethylene glycol. The shock drive pulse was incident on the back side at an angle of 60° to the normal to match the SFG probe pulses.

A block diagram of the Ti:sapphire laser system is shown in Fig. 2. The laser produces 3 mJ pulses 140 fs in duration at 1000 Hz. Part of the 800 nm laser output prior to compression is sent to an auxiliary compressor to generate a drive pulse with tunable duration 140 fs to 6 ps. The rest of the pulse generates fs IR and ps visible with a Fabry-Perot étalon filter.

Molecules used in the SAMs are depicted in Fig. 3. These molecules are energetic material (EM) simulants which mimic the functionalities found in nitroaromatic molecules, nitramines and nitrates. The circles indicate the part of the molecule probed by SFG. The rightmost three molecules in Fig. 3 simulate RDX, TNT, and

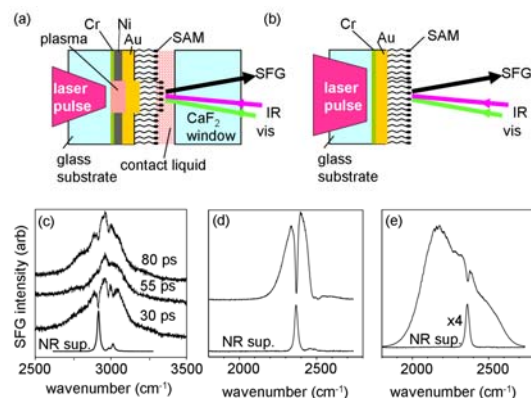


Figure 1. (a) Shock target array. (b) Heat shock target array. (c) SFG spectra of C18 SAM. The three small dips against the broad nonresonant (NR) background are the methyl head group CH-stretch transitions. The laser drive pulse arrives at $t = 0$. Shock arrival at ~ 50 ps causes the dips to lose intensity. (d) SFG spectra of 4-CN-benzenethiol in the heat shock configuration (b). (e) SFG of 4-CN-benzenethiol in the shock array configuration (a). A recent advance allows the NR backgrounds, even the larger background in (e) due to window and contact liquid, to be suppressed (NR sup.) leading to greatly improved signal-to-noise ratios.

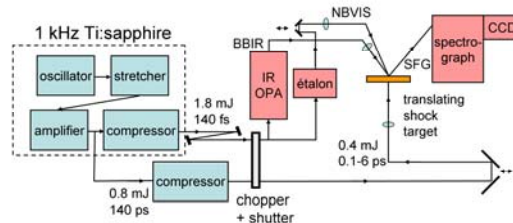


Figure 2. Block diagram of the laser apparatus. OPA: optical parametric amplifier; CCD: charge-coupled array detector.

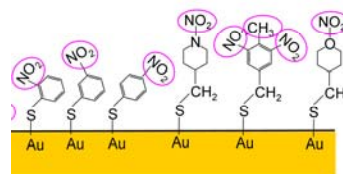


Figure 3. Structures of molecules used to grow SAMs in target arrays. SAMs are densely-packed 2D structures and we probe $\sim 10^{11}$ molecules on each shot. The circles indicate the functional groups monitored by SFG.

PETN. Most of these molecules were synthesized by an undergraduate, Aaron White, with help from postdoc Hiroki Fujiwara.

The dynamic shock experiments¹ were done in conjunction with measurements of the SAM spectra under conditions of static high pressure and (quasi) static high temperature. Temperatures reached during shock compression can be much greater than equilibrium temperatures for SAM decomposition, but we have developed a technique for flash-heating^{2,3} the Au layer to temperatures of several hundreds of degrees K. During the ~10 ns time period when the high temperature is constant, we can obtain the vibrational spectrum of the very hot SAM. For high pressures, we used a diamond anvil apparatus. Prior to our work it was not possible to obtain vibrational spectra of molecular monolayers in a diamond anvil because the quantity of molecules was too small. We developed tiny surface-enhanced Raman substrates that amplify the Raman spectrum by a factor of $>10^5$ for this purpose⁴. Figure 4 shows Raman spectra of a substituted benzene molecule monolayer in the diamond anvil. For nitroaromatic molecules, unfortunately the nitro resonances are overlapped by the intense diamond phonon Raman transition, so we have ordered SiN anvils which will not have this problem.

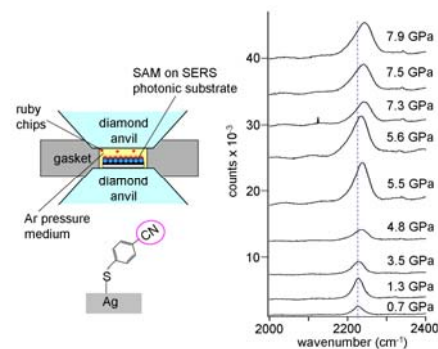


Figure 4. (left) Photonic chip in a diamond anvil cell provides surface-enhanced Raman scattering (SERS) by a factor of 10^6 . (right) Spectra obtained from 4-cyanobenzene SAM on Su (structure shown at left).

The SFG technique in broadband multiplex configuration can be sensitive enough to provide good vibrational spectra of monolayers. One problem is the nonresonant (NR) background that can hinder detection of vibrational transitions. Previously we studied 4 GPa shock compression of an 18-carbon alkanethiol (C18) SAM. Since SFG detects only molecular functionalities in noncentrosymmetric environments, with C18 in the CH-stretch region, SFG sees only the terminal methyl groups. As shown in Fig. 1c, the SFG spectrum consists of a broader NR background and three sharper dips. With a laser-drive pulse at $t = 0$, the shock front reaches the SAM at about 50 ps. When the front arrives, CH-stretch transitions lose intensity⁵. These spectra were of low quality due to low signal and NR background from the Au surface, the contact liquid and the CaF_2 window.

We recently made significant improvements in SFG. We increased the signal levels tenfold by increasing the pulse intensities and improving pulse focusing and we developed a NR suppression technique⁶. In the SFG output pulse the NR contribution appears in the first few hundred of fs while the resonant signal persists for 1-2 ps or so. Using a time-asymmetric time-delayed visible pulse, we suppressed the NR signal by time windowing to obtain much better C18 SAM spectra as in Fig. 1c.

A useful probe molecule is 4-cyanobenzene thiol (4CNB). The CN-stretch transition near 2350 cm^{-1} has a strong SFG signal in a spectral window where many other materials do not absorb. SFG spectra of 4CNB are shown in Fig. 1d, in the heat shock configuration. Adding the contact liquid and window increases the NR immensely, as shown in Fig. 1e, but we can still deeply suppress the NR.

In the heat shock technique, SFG probes a SAM after its Au substrate is flash-heated to generate a temperature jump of 600-800K. Results from heat shock and 4 GPa shock with a C18 SAM are compared in Figs. 5a and 5b. With C18 molecules, shock causes the SFG signal to decrease by bending the terminal methyl groups away from the surface normal. Heat shock causes a signal decrease by creating thermal disorder in the methyl group lattice. Figures 5a and 5b show the SFG signal decrease from 4 GPa shock and from 800K heat shock are very different. With the pump laser pulses arriving at $t = 0$, the shock response (Fig. 5a) is delayed by ~ 60 ps, representing the shock propagation through Ni and Au layers. The large SFG signal loss has a 4 ps rise time and an ~ 20 ps recovery that tracks shock unloading. The response to a 600K heat shock (Fig. 5b) is delayed just 1.5 ps from the laser pulse, the total SFG signal loss due to SAM disorder is smaller, and the disorder builds up with a 10 ps time constant. The Au surface remains at constant high temperature for 10 ns and cools to ambient on the 100 μ s time scale. The SAM reorders reversibly as the surface cools.

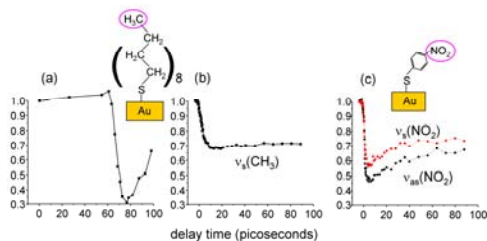


Figure 5. (a) SFG signal loss of CH-stretch of C18 SAM from a 4 GPa shock generated by a laser at $t = 0$. (b) SFG signal loss from C18 SAM by 600K heat shock. (c) SFG signal from nitro groups after heat shock.

In the C18 heat shock, the 1.5 ps delay time represents the time needed for the leading edge of the heat burst to propagate from the Au surface, along the alkane chains, to the methyl groups probed by SFG. In experiments where the chain length was varied from 1.2 to 3.5 nm (6 to 24 carbon atoms), this delay time was a linear function of chain length, showing that heat flow along the alkane chains was ballistic with a velocity of 1 km/s. The ballistic heat propagation along alkane chains is the reason why we refer to these experiments as "heat shock" rather than ordinary heat conduction. Ordinary conduction would be diffusive rather than ballistic. Ballistic heat transport occurs due to the short propagation distance. Heat shock data obtained from nitrobenzene SAMs are shown in Fig. 5c, where we probed the symmetric $\nu_s(\text{NO}_2)$ and antisymmetric $\nu_a(\text{NO}_2)$ nitro transitions (1450 and 1600 cm^{-1} respectively). These data illustrate our ability to directly probe heat shock excitation of aromatic nitro groups².

Summary. Shock compression and heat shock in molecular monolayers allow us to study ultrafast molecular response with atomic scale time and space resolution. We have greatly improved SFG detection sensitivity and suppressed the NR background. We directly measured the velocity of heat shock propagation along alkane chains. We developed a photonic substrate to amplify SAM Raman spectra so we can measure the pressure shift in a DAC. We have developed SAMs that function as energetic material simulants and we have studied their heat shock response.

One of the most significant issues in ultrafast shock compression studies of energetic materials has been how to get enough shock compression to see significant chemical reactivity on short time scales. So far neither a 4 GPa shock nor a 800K temperature jump creates significant chemical reactivity. However it should be possible soon to combine these techniques, with a high temperature preheat followed by a shock wave.

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